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(54) DETERGENT ARTICLE FOR USE IN AUTOMATIC DISHWASHER

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Abstract of the Disclosure

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A detergent article for use in an automatic dishwasher, consisting essentially of a paste-form detergent composition contained in a packet made of a water-soluble film, is disclosed. A process for washing tableware and cookware utilizing these detergent articles in an automatic dishwasher is also described.

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Background of the Invention

It has long been known that detergent formulations in paste or liquid form offer advantages to the consumer which conventional granular or powder-form detergent compositions cannot offer. The most important of these advantages is that such paste or liquid compositions may be sold in concentrated form, so that the consumer may use a smaller, more manageable amount of the composition for each wash load and does not have to contend with the storage of large volumes of the composition when it is not in use.

A wide variety of such types of detergent compositions has been disclosed for use in the laundering of soiled fabrics. For example, French Patent 1,602,442, Henkel & Cie, GmbH, issued December 31, 1970, relates to a laundry detergent composition having a paste form, while German Patent 2,226,925, Kao Soap Company, Ltd., discloses laundry detergent compositions in gel form, and Canadian Patent 1,020,039,

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Collins et al, issued November 1, 1977, relates to laundry detergent compositions in liquid form. Since laundry detergent compositions are usually mixed directly with the wash water the first time in the washing cycle that the automatic washing machine is filled up, the use of such paste or liquid detergent compositions does not present any dispensing problem when used in a conventional automatic clothes washing machine.

However, because of the nature of the washing process and the structure of certain types of automatic dishwashers, problems may be encountered when automatic dishwasher detergent compositions are formulated in a paste or liquid form. In double dispensing cup type automatic dishwashers, the detergent composition to be used in the washing process is loaded into an automatic dispenser in the machine prior to the start of the washing cycle. Once the washing cycle is started, the dirty tableware is subjected to a rinse step, prior to the introduction of the detergent into the washing system. After the water rinse is completed, the detergent dispenser cup opens, the detergent composition is released into the washing system, and the tableware is washed in an aqueous solution of the detergent composition.

Because the detergent dispensers in dishwashers are generally not constructed to be water-tight, the use of a liquid detergent composition in such a dispenser would result in the detergent composition running out of the dispenser during the rinse cycle, leaving no detergent present when the dispenser cup opens at the start of the wash cycle. As a result of its higher viscosity, a paste detergent composition would not be subject to this problem and, hence, would be suitable for use in this type of automatic

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dishwasher. Consequently, paste-form detergent compositions for use in automatic dishwashers have been disclosed. For example, U.S. Patent 4,123,395, Maguire et al, issued October 31, 1978; U.S. Patent 4,101,457, Place et al, issued July 18, 1978, Canadian Patent 1,073,381, Maguire et al, issued March 11, 1980; U.S. Patent 4,090,973, Maguire et al, issued May 29, 1978, and German Patent 2,038,103, Henkel & Cie, GmbH, issued February 10, 1972, all disclose such paste-form detergent compositions.

Although the higher viscosity of the paste compositions does eliminate the composition leakage problem which may be present when liquid detergent compositions are used in automatic dishwashers, such compositions tend to dispense out of the dispenser cup very slowly during the wash cycle and, hence, are slow to become solubilized in the aqueous wash solution. The fact that the full amount of the detergent composition, placed in the dishwashing machine, takes a longer time to get into the washing solution, decreases the overall effectiveness of the washing process.

It is therefore an object of this invention to formulate paste-form detergent composition articles for use in automatic dishwashers, which give effective cleaning of tableware and cookware together with efficient release from the detergent dispenser and effective solubilization into the aqueous washing solution.

It is a further object of this invention to formulate paste-form detergent composition articles for use in automatic dishwashers which provide ease of handling and dispensing for the user.

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It is a still further object of this invention to produce paste-form detergent composition articles which minimize the hygiene and safety problems which may accompany the use of concentrated detergent compositions.

It is also an object of this invention to provide a method for cleaning tableware and cookware in an automatic dishwasher utilizing the paste-form detergent composition articles of the present invention.

Summary of the Invention

In accordance with the present invention there is provided an article for cleaning tableware and cookware in an automatic dishwasher, consisting essentially of a packet made up of a water-soluble material in film form, enclosing within it a paste-form, automatic dishwasher-compatible detergent composition.

It has been found that by including these paste-form detergent compositions in packets made of a water-soluble material, which may be added directly to the detergent dispenser of the automatic dishwasher, the dispensing and solubilization problems can be eliminated, while still retaining the benefits which the paste-form compositions offer. In addition, the use of the detergent compositions in such packets provides easy handling of the compositions for the consumer and minimizes user contact with any alkaline or enzyme ingredients which the compositions may contain.

The water-soluble packet is preferably made from polyvinyl alcohol, polyethylene oxide, or methyl cellulose. It is also preferred that the detergent compositions contained in the

packet comprise an ethoxylated or propoxylated nonionic surface-active agent. The detergent composition may also contain additional components which are often found in detergent compositions for use in automatic dishwashers, such as organic and inorganic detergent builder ingredients, alkali materials, sequestering agents, china protecting agents, hydrotropes, corrosion inhibitors, drainage promoting ingredients, dyes, and perfumes. Preferred detergent compositions for use in the articles of the present invention contain suds suppressing components and/or high alkaline activity, amylolytic or proteolytic enzymes.

A process for cleaning soiled tableware and cookware in an automatic dishwasher, utilizing the detergent articles of the present invention is also taught herein.

Detailed Description of the Invention

The detergent articles of the present invention consist essentially of a packet made of a water-soluble or water-dispersible film enclosing within it a paste-form detergent composition, which will not dissolve said film, formulated for use in an automatic dishwasher. The components of the articles of this invention will be discussed in detail hereinafter.

The detergent compositions used in the articles of the present invention are in the form of a paste, and are suitable for use in an automatic dishwasher. These paste-form detergent compositions generally have viscosities of about 5,000 centipoise, but which can range up to several hundred million centipoise. As used herein, the term "paste" is intended to encompass paste, gel, and viscous liquid detergent

compositions having a minimum viscosity of at least about 1000 centipoise, preferably at least about 2,000 centipoise.

The detergent compositions must exhibit certain performance characteristics to make them suitable for use in an automatic dishwasher. The compositions should be formulated so as to be relatively low sudsing in use. If a composition tends to form excessive amounts of suds during the dishwashing process, the mechanical operation of the dishwashing machine can be impaired due to a lowering of the pressure at which the washing liquid is forced against the hard surfaces to be washed. This condition can be met by the proper selection of the composition's surfactant system or by the inclusion of a suds-regulating agent in the detergent composition. The composition should also be effective in the removal of various classes of food soils, particularly proteinaceous, greasy, and fatty soils. The detergent composition must also be sufficiently water-soluble or water-dispersible at the 110°F to 150°F dishwasher water temperatures, so as to assure a sufficient amount of the composition in the washing system during the dishwasher cycle. Finally, the detergent compositions should have a pH, in use, of from about 8.5 to 11.5, preferably from about 9 to 11, and most preferably from about 9.5 to 10.5.

A large variety of detergent compositions for use in automatic dishwashers may be formulated as pastes. Examples of such compositions are disclosed in the above mentioned U.S. Patents 4,123,395; 4,101,457 and 4,090,973 and Canadian patent 1,073,381.

In addition, other automatic dishwasher detergent formulations, which are usually made in granular or powder form, may also be formulated as pastes, as long as any incompatible components are not included. Examples of such compositions are disclosed in Canadian Patent 966,751, benson et al, issued April 29, 1975, Canadian Patent Application Serial No. 218,740, Lagasse et al, filed January 27, 1975; U.S. Patent 3,598,743, Coates, issued August 10, 1971; U.S. Patent 3,544,473, Kitchen et al, issued December 1, 1970; and U.S. Patent 3,630,923, Simmons et al, issued December 28, 1971.

The detergent compositions used in the articles of the present invention may contain water-soluble anionic or nonionic surface-active agents. Anionic surfactants may be used in conjunction with a suds-suppressing agent, so as to control the sudsing characteristics of the entire composition. Anionic surfactants known in the detergency arts may be used in the compositions herein. Examples of such surfactants are listed in U.S. Patent 3,717,630, Booth, issued February 20, 1973, and U.S. Patent 3,332,880, Kessler et al, issued July 25, 1967. A preferred type of anionic surfactant is disclosed in U.S. Patent 3,941,710, Gilbert et al, issued March 2, 1976.

Preferred compositions for use in the articles of the present invention contain a nonionic surface-active agent, particularly an alkoxylated nonionic surface-active agent, wherein the alkoxy moiety is ethylene oxide, propylene oxide, or mixtures thereof. The surface-active component should comprise

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at least about 0.5% by weight of the detergent composition. However, by choosing an appropriate nonionic surfactant system, along with small quantities of materials such as solubilizers, thickeners, and the like, stable paste-form compositions containing up to about 55% of the nonionic surfactant system may be prepared. Preferred detergent compositions contain from about 1 to about 40% of the nonionic surfactant, most preferably from about 3 to about 30%.

Most commonly, nonionic surfactants are compounds produced by the condensation of an alkylene oxide, especially ethylene oxide (hydrophilic in nature) with an organic hydrophobic compound, which is usually aliphatic or alkyl aromatic in nature. The length of the hydrophilic polyoxyalkylene moiety which is condensed with any particular hydrophobic compound can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic properties. A typical listing of classes and species of such nonionic surfactants useful herein appears in U.S. Patent 3,664,961.

Preferred nonionic surface-active agents include alkoxylated nonionic surfactants wherein the alkoxy moiety is selected from the group consisting of ethylene oxide, propylene oxide, and mixtures thereof. Ethylene oxide represents the preferred condensation partner. The alkylene oxide moiety is condensed with a nonionic-based material according to techniques known in the art. All alkoxylated nonionic detergents which are normally known to be suitable for use in detergent technology can be used herein. Examples of such components include:

(1) The condensation product of one mole of a saturated or unsaturated, straight or branched chain carboxylic acid having from about 10 to about 18 carbon atoms with from about 5 to about 50 moles of ethylene oxide. The acid moiety can consist of mixtures of acids in the above-delineated carbon atoms range or it can consist of an acid having a specific number of carbon atoms within this range. The condensation product of one mole of coconut fatty acid having the approximate carbon chain length distribution of 2% C_{10}, 66% C_{12}, 23% C_{14}, and 9% C_{16} with 35 moles of ethylene oxide is a specific example of a nonionic containing a mixture of different chain lengths fatty acid moieties. Other specific examples of nonionics of this type are: the condensation product of one mole of palmitic acid with 40 moles of ethylene oxide; the condensation product of one mole of myristic acid with 35 moles of ethylene oxide; the condensation product of one mole of oleic acid with 5 moles of ethylene oxide; and the condensation product of one mole of stearic acid with 30 moles of ethylene oxide.

(2) The condensation products of one mole of a saturated or unsaturated, straight or branched chain alcohol having from about 10 to about 24 carbon atoms with from about 5 to about 50 moles of ethylene oxide. The alcohol moiety can consist of mixtures of alcohols in the above-delineated carbon atom range or it can consist of an alcohol having a specific number of carbon atoms within this range. The condensation product of one mole of coconut alcohol having the approximate chain length distribution of 2% C_{10}, 66% C_{12}, 23% C_{14}, and 9% C_{16} with 45 moles of ethylene

oxide is a specific example of a nonionic containing a mixture of different chain length alcohol moieties. Other specific examples of nonionics of this type are the condensation products of one mole of tallow alcohol with 9 and 20 moles of ethylene oxide respectively; the condensation products of one mole of lauryl alcohol with 35 moles of ethylene oxide; the condensation products of one mole of myristyl alcohol with 30 moles of ethylene oxide; and the condensation products of one mole of oleyl alcohol with 40 moles of ethylene oxide.

(3) Polyethylene glycols having a molecular weight of from about 400 to about 30,000. For example, Dow Chemical Company manufactures these nonionics in molecular weights of 20,000, 9500, 7500, 4500, 3400, and 1450, all of which are waxlike solids which melt between 110°F and 200°F.

(4) The condensation products of one mole of alkyl phenol wherein the alkyl chain contains from about 8 to about 18 carbon atoms with from about 4 to about 50 moles of ethylene oxide. Specific examples of these nonionics are the condensation products of one mole of decyl phenol with 40 moles of ethylene oxide; the condensation products of one mole of dodecyl phenol with 35 moles of ethylene oxide; the condensation products of one mole of tetradecyl phenol with 35 moles of ethylene oxide; and the condensation products of one mole of hexadecyl phenol with 30 moles of ethylene oxide.

(5) The ethoxylated surfactants disclosed in U.S. Patent Application Serial Number 557,217, filed March 10, 1975, inventor Jerome H. Collins, ~~incorporated herein by~~

~~reference,~~ consisting essentially of a mixture of compounds having at least two levels of ethylene oxide addition and having the formula: $R_1 - R_2 - O(CH_2CH_2O)_nH$, wherein R_1 is a linear alkyl residue and R_2 has the formula $-CHR_3CH_2-$ wherein R_3 is selected from the group consisting of hydrogen and mixtures thereof with not more than 40% by weight of lower alkyl, wherein R_1 and R_2 together form an alkyl residue having a mean chain length in the range of 8-15 carbon atoms, at least 65% by weight of said residue having a chain length within $\pm$ 1 carbon atom of the mean, wherein $3.5<n<6.5$, provided that the total amount of components in which $n = 0$ is not greater than 5% by weight and the total amount of components in which $n = 2-7$ inclusive is not less than 63% by weight, and the hydrophilic-lipophilic balance (HLB) of said ethoxylate material is in the range from 9.5-11.5, said surfactant composition being otherwise free of nonionic surfactants having an HLB outside of said range.

Low-foaming alkoxylated nonionic surfactants are preferred for use in the detergent compositions, although nonionics which do not exhibit low-foaming properties can be used without departing from the spirit of this invention, as long as they are used in conjunction with a suds-regulating agent so as to control the foaming characteristics of the detergent composition as a whole. Examples of nonionic low-foaming surface-active components include: the condensation products of benzyl chloride and an ethoxylated alkyl phenol wherein the alkyl group has from about 6 to about 12 carbon atoms and wherein from about 12 to about 20 ethylene oxide molecules have been condensed per mole of alkyl phenol; polyetheresters of the formula

$(ClC_6H_4)_2CHCO_2(CH_2.CH_2.O)_xR$

wherein x is an integer from 4 to 20 and R is a lower alkyl group containing not more than 4 carbon atoms, for example a component having the formula

$(ClC_6H_4)_2CHCO_2(CH_2CH_2O)_{15}.CH_3$;

the polyalkoxylation products of alkyl phenol, for example, the polyglycol alkyl phenol ethers containing an alkyl group having at least 6 and, normally, from about 8 to about 20 carbon atoms and having a molar ratio of ethylene oxide to condensate of about 7.5; 9.0; 11.5; 20.5; and 30. The alkyl group can, for example, be represented by diisobutylene; di-amyl; polymerized propylene; iso-octyl; and nonyl.

Additional examples of effective low-foaming nonionics include: the polyalkylene glycol condensates disclosed in U.S. Patent 3,048,548, having alternating hydrophilic oxyethylene chains and hydrophobic oxypropylene chains wherein the weight of the terminal hydrophobic chains, the weight of the middle hydrophobic unit and the weight of the linking hydrophilic units each represent about 1/3 of the condensate; the de-foaming nonionic surfactants disclosed in U.S. Patent 3,382,178, having the general formula $Z[(OR)_nOH]_z$ wherein Z is alkoxylatable material, R is a radical derived from an alkylene oxide which can be ethylene and propylene and n is an integer from, for example, 10 to 2000 or more and z is an integer determined by the number of reactive oxyalkylatable groups. Z can be represented by normal

biodegradable alcohols such as, for example, those obtained by reduction of fatty acids derived from coconut oil, palm kernel oil, tallow and also those obtained from petroleum such as, for example, the mixtures of C_{10} to C_{18} straight-chain primary alcohols; the nonionic surface-active agents of U.S. Patent 3,549,539 being a mixture of nonylphenol-5-EO or the condensation product of a random C_{11} to C_{15} secondary alcohol and ethylene oxide having an HLB value between 11.5 and 13.5; and a polyethylene oxide/polypropylene oxide condensate that consists of between 5 and 25% polyethylene oxide and 95 and 75% polypropylene oxide and has a molecular weight between 1500 and 2700; the conjugated polyoxyalkylene compounds described in U.S. Patent 2,677,700, corresponding to the formula:

$$Y(C_3H_6O)_n(C_2H_4O)_mH$$

wherein Y is the residue of organic compounds having from about 1 to 6 carbon atoms and at least one reactive hydrogen atom, n has an average value of at least about 6.4, as determined by hydroxyl number and m has a value such that the oxyethylene portion constitutes about 10 to 90 weight percent of the molecule; the conjugated polyoxyalkylene compounds described in U.S. Patent 2,674,619, incorporated herein by reference, having the formula:

$$Y[(C_3H_6O)_n(C_2H_4O)_mH]_x$$

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wherein Y is the residue of organic compounds having from about 2 to 6 carbon atoms and containing x reactive hydrogen atoms in which x has a value of at least about 2, n has a value such that the molecular weight of the polyoxypropylene hydrophobic base is at least about 900 and m has a value such that the oxyethylene content of the molecule is from about 10 to 90 weight percent. Compounds falling within the scope of the definition for Y include, for example, propylene glycol, glycerine, pentaerythritol, trimethylolpropane, ethylenediamine and the like. The oxypropylene chains optionally, but advantageously, contain small amounts of ethylene oxide and the oxyethylene chains also optionally, but advantageously, contain small amounts of propylene oxide.

Additional conjugated polyoxyalkylene surface-active agents which are advantageously used in the compositions of this invention correspond to the formula:

$$P[(C_3H_6O)_n(C_2H_4O)_mH]_x$$

wherein P is the residue of organic compounds having from about 8 to 18 carbon atoms and containing x reactive hydrogen atoms in which x has a value of 1 or 2, n has a value such that the molecular weight of the polyoxypropylene portion is at least about 58 and m has a value such that the oxyethylene content of the molecule is from about 10 to 90 weight percent and the formula:

$$P[(C_2H_4O)_n(C_3H_6O)_mH]_x$$

wherein P is the residue of an organic compound having from about 8 to 18 carbon atoms and containing x reactive hydrogen atoms in which x has a value of 1 or 2, n has a value such that the molecular weight of the polyoxyethylene portion is at least about 44 and m has a value such that the oxypropylene content of the molecule is from about 10 to 90 weight percent. In either case the oxypropylene chains may contain optionally, but advantageously, small amounts of ethylene oxide and the oxyethylene chains may contain also optionally, but advantageously, small amounts of propylene oxide.

Preferred nonionic surfactants for use in the present invention include the mono- and polyalkoxy-substituted surfactants having the terminal hydroxyl of the alkoxy group acylated by certain monobasic acids ("capped" surfactants), described in U.S. Patent 4,088,598, Williams, issued May 9, 1978.

Highly preferred alkoxylated nonionics for use herein include the condensation product of one mole of tallow alcohol with from about 6 to about 20 moles, especially 9 moles, of ethylene oxide; the alkoxylate commercially available under the trademark PLURADOT HA-433® Wyandotte Chemical Corp., which has a molecular weight in the range from 3700-4200 and contains about 3% monostearyl acid phosphate suds suppressor;

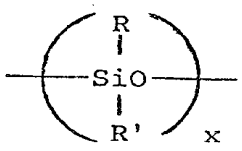
and also the condensation product of C_{14-15} alcohol with from 5 to 17 moles particularly 7-9 moles, of ethylene oxide. An example of such a surfactant is commercially available as NEODOL ^{R} 45-7, available from Shell Chemical Corp., which is the condensation product of C_{14-15} alcohol with 7 moles of ethylene oxide per molecule of alcohol.

The compositions for use in the articles of this invention may also comprise a suds-regulating agent for the purpose of controlling the sudsing of the composition during use. Excessive sudsing can have the effect of decreasing the efficiency of the dishwashing machine and, hence should be avoided. The final selection of the suds-suppressing agent depends, at least in part, upon the qualitative and quantitative characteristics of the particular surface-active agent which is utilized in the detergent composition. Suds-regulating agents are particularly useful in automatic dishwashing detergent compositions since some types of food residues, especially proteinaceous food residues, exhibit suds-boosting properties.

Suds-regulating components are normally used in an amount of from about 0.001% to about 5%, preferably from about 0.05% to about 3%, and especially from about 0.1% to about 1%. Suds-suppressing agents known in the art to be suitable for use in the detergent context are useful in the compositions herein.

Preferred suds-suppressing additives are described in U.S. Patent 3,933,672, Bartolotta et al, issued January 20, 1976, relating to silicone suds-controlling agents. The silicone material can be represented by alkylated polysiloxane materials such as silica aerogels and xerogels, and hydrophobic silicas of

various types. The silicone material may be described as a siloxane having the formula:



wherein x is from about 20 to about 2,000 and R and R' are each alkyl or aryl groups, especially methyl, ethyl, propyl, butyl, and phenyl. The polydimethyl siloxanes (R and R' are methyl) having a molecular weight within the range of from about 200 to 200,000, and higher, are all useful as suds controlling agents. Additional suitable silicone materials, wherein the side chain groups are R and R' are alkyl, aryl, or mixed alkyl and aryl hydrocarbyl groups, exhibit useful suds controlling properties. Examples of such ingredients include diethyl-, dipropyl-, dibutyl-, metyl and ethyl-, phenylmethyl polysiloxanes and the like. Additional useful silicone suds controlling agents can be represented by a mixture of an alkylated siloxane, as referred to above, and solid silica. Such mixtures are prepared by affixing the silicone to the surface of the solid silica. A preferred silicone suds controlling agent is represented by a hydrophobic silanated (most preferably trimethylsilanated) silica having a particle size in the range of from about 10 millimicrons to 20 millimicrons in a specific surface area above about 50 square meters per gram, intimately admixed with dimethyl silicone fluid having a molecular weight in the range of from about 500 to about 200,000 at a weight ratio of silicone to

silanated silica of from about 19:1 to about 1:2. The silicone suds suppressing agent is advantageously releaseably incorporated in a water-soluble or water-dispersible, substantially nonsurface-active detergent-impermeable carrier.

Particularly useful suds-suppressors are the self-emulsified silicone suds-suppressors described in Canadian Patent Application Serial No. 263,320, Gault et al, filed October 13, 1976. An example of such a compound is DB-544, which is a mixture of silica, an alkoxylated siloxane, and a siloxane/glycol copolymer, and is commercially available from Dow Corning.

Microcrystalline waxes having a melting point in the range of from 35°C to 115°C and a saponification value less than 100, represent an additional example of a preferred suds regulating component for use in the subject compositions. The microcrystalline waxes are substantially water-insoluble, but are water-dispersible in the presence of organic surfactants. Preferred microcrystalline waxes have a melting point of from about 65°C to 100°C, a molecular weight in the range of 400 to 1000, and a penetration value of at least 6, measured at 77°F by ASTM-D1321. Suitable examples of the above waxes include: microcrystalline and oxidized microcrystalline petrolatum waxes; Fischer-Tropsch and oxidized Fischer-Tropsch waxes; ozokerite; ceresin; montan wax; beeswax; candelilla; and carnauba wax.

Alkyl phosphate esters represent an additional preferred suds suppressant for use herein. These preferred phosphate esters are predominantly monostearyl acid phosphate which, in addition thereto, can contain di- and tristearyl phosphates and monooleyl phosphates, which can contain di and trioleyl phosphates.

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The alkyl phosphate esters frequently contain some trialkyl phosphate. Accordingly, a preferred phosphate ester can contain, in addition to the monoalkyl ester, e.g., monostearyl phosphate, up to about 50 mole percent of dialkyl phosphate and up to about 5 mole percent of trialkyl phosphate.

The dishwasher-compatible detergent compositions useful in the present invention may also contain an enzyme component. The enzymes aid and augment the removal of soils from the objects to be cleaned. This enzymatic action may result from a series of individual chemical reactions, such as hydrolysis, oxidation and substitution reactions.

Because the detergent compositions useful herein have a relatively high in-use pH, the enzymes which are most useful in the detergent compositions are those which exhibit a high degree of enzymatic activity in highly alkaline systems. Thus, the preferred enzymes are high alkaline activity proteases, high alkaline activity amylases, and mixtures thereof. Preferred proteolytic enzymes are those which exhibit a proteolytic activity of 80 to 100% of maximum activity when measured at pH 12 using the Anson Hemoglobin method carried out in the presence of urea. Examples of this type of proteolytic enzyme are described in British Patent Specification 1,361,686, and correspond to bacterium strains which have been deposited at the National Collection of Industrial Bacteria (NCIB), Torry Research Station, Aberdeen, Scotland, and are produced by the bacterium strains numbered NCIB 10317, NCIB 10147, NCIB 10313, and NCIB 10315. Another preferred proteolytic enzyme is that

cultivated from the microorganism Bacillus Firmus strain NRS 783, as described in U.S. Patent 3,827,938, Aunstrup et al, issued August 6, 1974. This

strain of Bacillus Firmus may be obtained from the U.S. Department of Agriculture, Agricultural Research Service, Peoria, Illinois, as strain NRRL B 1107. Preferred commercially available protecolytic enzymes for use in these detergent compositions, are available under the tradenames SP-72 (Experase®) and SP-88, produced and marketed by Novo Industri A/S, Copenhagen, Denmark.

Preferred amylolytic enzymes are those which exhibit an amylolytic activity of greater than 50% of maximum activity when measured at pH 8 by the SKB method at 37°C.

Commercially available examples of such amylolytic enzymes include Monsanto® DA-10, available from Monsanto; Rapidase®, available from Societe Rapidase, France; Milezyme®, available from Miles Laboratories, Elkhart, Indiana; and Ban®, available from Novo Industri A/S, Denmark. Particularly preferred amylolytic enzymes are those described in British Patent Specification 1,296,839, cultivated from the strains of Bacillus Lichenformis NCIB 8061, NCIB 8059; ATCC (America type culture collection) 6334; ATCC 6598; ATCC 11945; ATCC 8480; ATCC 9945A. A particularly preferred, commercially available amylolytic enzyme, is produced and distributed under the tradename SP-95 (Termamyl®), by Novo Industri A/S, Copenhagen, Denmark.

In a particularly preferred embodiment, the enzyme component consists of a mixture of the preferred proteolytic and preferred amylolytic enzymes, disclosed above, in a ratio of from about 4:1 to 1:4 by weight, preferably from about 2:1 to about 1:2, and most preferably in a ratio of about 1:1. The preferred proteolytic, amylolytic and enzyme mixture components discussed above are disclosed and defined in U.S. Patent 4,090,973, Maguire et al, issued May 29, 1978.

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The enzyme component is included in the detergent compositions in an amount effective to provide beneficial cleaning properties in an automatic dishwasher context. It is preferred that the enzymes be used in an amount such that the final cleaning composition has an amylolytic activity of at least 150 kilo Novo units per kilogram and/or a proteolytic activity of at least 6.0 Anson units per kilogram. This corresponds roughly to detergent compositions comprising from about 0.001% to about 5% by weight, of the enzyme component, utilizing generally available commercial enzyme preparations. Most preferably, this corresponds to detergent compositions comprising from about 0.1% to about 1.5% by weight of the enzyme component. The enzymes used in the detergent compositions may, for stability reasons, be encapsulated with a nonionic surface-active material, as described in U.S. Patent 4,090,973.

In addition to the components described hereinbefore, the detergent compositions used in the articles of the present invention can contain additional ingredients which are known to be suitble for use in automatic dishwashing compositions, in the art-established levels for their known functions. Organic and inorganic detergent builder ingredients, alkali materials, sequestering agents, china-protecting agents, reducing agents, hydrotropes, corrosion inhibitors, soil-suspending ingredients, drainage promoting ingredients, enzyme-stabilizing aids, dyes, perfumes, fillers, crystal modifiers and the like represent examples of functional classes of additional automatic dishwashing composition additives.

Suitable inorganic builders include polyphosphates, for example, tripolyphosphate, pyrophosphate, or metaphosphate, carbonates, bicarbonates, and alkali silicates. Particularly preferred are the sodium and potassium salts of the aforementioned inorganic builders. Examples of water-soluble organic builder components include the alkali metal salts of polyacetates, carboxylates, polycarboxylates, and polyhydroxysulfonates. Additional examples include sodium citrate, sodium oxydisuccinate, and sodium mellitate. Normally these builder ingredients can be used in amounts of up to 60%, preferably in the range of from about 10 to 50% by weight.

In order to provide satisfactory pasty compositions, up to about 60% of a solvent, solubilizing material, or suspending agent may be included. Examples of preferred components of this type include polyethylene glycol having a molecular weight of about 400, triethanolamine, methyl esters, C_{12-13} alcohols commercially available as NEODOL® 23 alcohols from Shell Chemical Corp., and mixtures thereof. Water may be used in this context and forms the continuous phase of a concentrated dispersion, however, preferred compositions for use herein are essentially anhydrous. In many cases, it is desirable to include a viscosity control agent or a thixotropic agent to provide a suitable product form. For example, aqueous solutions or dispersions may be thickened or made thixotropic by the use of conventional agents such as methylcellulose, carboxymethylcellulose, starch, polyvinylpyrrolidone, gelatin, colloidal silica, natural or synthetic clay materials and the like.

To make the detergent articles of the present invention, a dishwasher-compatible detergent composition, such as those described above, is enclosed in a packet made up of a water-soluble

material in film form. As used herein, the term "water-soluble film" is intended to include those films which are water-dispersible, as well as those which are water-soluble. Each packet may contain a premeasured amount of the detergent composition suitable for a single washing load in an automatic dishwasher, or a convenient fraction of such an amount. It is preferred that the packets contain from about 2 to 50 grams, most preferably from about 5 to about 20 grams, of the detergent composition. In addition, the packet should be of a convenient size so as to fit, either folded or unfolded, into the detergent dispenser cup of an automatic dishwasher.

A film suitable for use in making packets of the foregoing type must be rapidly and completely soluble or dispersible in hot water ranging in temperature from about 110 to about 150°F, particularly about 120°F. It must be strong, tough, flexible, shock-resistant and nontacky during storage at both high and low temperatures and humidity. Very importantly, these properties must be retained by the film while it is in contact with the alkaline detergent compositions used in the present invention. In choosing a film, it is important that the one chosen is compatible with the components of the detergent composition to be contained in the article. This compatibility is particularly important in terms of the solvent, described above, used in the detergent composition. For example, where the detergent composition contains water as its solvent, the film chosen must be one which will readily solubilize in the 110-150°F dishwasher water, but which will not be solubilized, during storage, by the water in the composition. The film used

to make the packets should have a thickness of from about 0.5 to 5 mils, preferably from about 1 to 3 mils, and most preferably about 1.5 mils.

It is, furthermore, very desirable that the water-soluble film be readily self-sealable, especially by heat, heat and water, or ultrasonic sealing methods. The sealed portions should dissolve well, along with the remainder of the packets. Preferably, the film should seal completely and permanently at a relatively low temperature and in a short period of time.

Examples of materials useful in making the packets of the present invention include modified starches, methyl and hydroxy propylmethylcellulose derivatives, hydroxyethyl cellulose, carboxymethylcellulose, polyvinyl alcohols, such as those described in U.S. Patent 3,413,229, Bianco et al, issued November 26, 1968; U.S. Patent 3,277,009, Freifeld et al, issued October 4, 1966; and U.S. Patent 3,300,546, Baechtold, issued January 24, 1967, polyvinylpyrrolidone, and ethylene oxide polymers. These materials are discussed in detail in Water Soluble Resins, Davidson and Sittig, Van Nostrand Reinhold Co., 1968. Preferred materials for making the packets include polyvinyl alcohol, polyethylene oxide, and methylcellulose.

The detergent articles of the present invention are utilized by placing them inside of an automatic dishwasher prior to the start of the dishwashing cycle, in the place of ordinary dishwasher detergent compositions. It is preferred that the detergent articles are placed inside the detergent dispenser cup of the automatic dishwasher.

The following nonlimiting examples illustrate the articles and methods of the present invention.

EXAMPLE I

A paste-form detergent composition suitable for use in automatic dishwashers, having the components set forth below, was formulated using conventional methods. The composition had a viscosity of about 500,000 centipoise.

Component	% by weight
Sodium tripolyphosphate	24.1
P_2O_5	10.6
Silicate solids (4:1 ratio by weight of 2.4r:2.0r)	17.0
SiO_2	11.9
Water	8.5
Neodol 45-7[1]	4.2
Triethanolamine	19.0
Dye	1.0
Perfume	0.2
SAG 100[2]	0.7
SP-88[3] (in polyethylene glycol 6000 prills)	1.2
Termamyl[4] (in polyethylene glycol 6000 prills)	1.6

[1]Condensation product of one mole of C_{14-15} alcohol with 7 moles of ethylene oxide.

[2]A polydimethylsiloxane silica suds suppressor, commercially available from Dow Corning.

[3]A proteolytic enzyme, commercially available from Novo Industri A/S, Copenhagen, Denmark, which exhibits an activity of greater than 80% of its maximum activity when measured at pH 12 using the Anson hemoglobin method in the presence of urea.

[4]An amylolytic enzyme, commercially available from Novo Industri A/S, Copenhagen, Denmark, which exhibits an activity of greater than 50% of its maximum activity when measured at pH 8 by the SKB method at 37°C.

Article A was made by heat-sealing about 12 grams of the above composition in a 5cm. square packet made out of a medium hydrolysis polyvinyl alcohol film, commercially available from Monosol, having a thickness of about 1.5 mils. Article B was made by heat-sealing about 12 grams of the above composition in a 5cm. square packet made out of Edisol-M, a methyl cellulose film, having a thickness of about 1.5 mils, commercially available from Polymer Films, Inc.

Each of the above articles was placed in the detergent dispenser cup of a Frigidaire automatic dishwasher, and the amount of time which it took for the article and the enclosed composition to completely dissolve in the washing solution during the washing cycle, after the dispenser cup opened, was determined. Each composition was tested in water temperatures of 130°F and 140°F, with a water hardness of 15 grains/gallon. As a control, the same tests were carried out using 12 gram portions of the

above paste composition, which were placed directly into the detergent dispenser cup of the dishwasher. The results obtained are summarized in the table below.

Article	Dissolution Time (seconds)	
Water Temperature	130°F	140°F
A	30	30
B	30	45
Control	90	90

The data above indicate that the inclusion of the paste-form detergent compositions in the water-soluble packets, increased the rates at which the paste compositions were dispensed out of the dishwasher dispenser cup and were dissolved into the aqueous washing solution, during the automatic dishwasher cleaning cycle.

Substantially similar results are obtained when the nonionic surfactant of Example I is substituted with the condensation product of tallow alcohol with about 9 moles of ethylene oxide (TAE_9), or an ethylene oxide/propylene oxide condensate of trimethylol propane (commercially available from Wyandotte as Pluradot® HA-433), or with a similar surfactant substituted with a substantially identical alkoxylate containing, instead of the trimethylol propane radical, an alkalol selected from the group consisting of propylene glycol, glycerine, pentaerythritol, and ethylenediamine.

Similar results are also obtained where the water-soluble film used to make the packets is polyethylene oxide, hydroxyethylcellulose, carboxymethylcellulose or a hydroxy propylmethylcellulose derivative.

Excellent performance is also obtained when the suds suppressor, used above, is replaced by a silicone suds suppressor selected from the group consisting of trimethyl-, diethyl-, dipropyl-, dibutyl-, methylethyl-, and phenylmethylpolysiloxane and mixtures thereof, in an amount ranging from about 0.1% to about 0.5%. Similar results are also obtained by using monostearyl acid phosphate suds suppressor, or a self-emulsified silicone suds suppressor, such as DB-544, commercially available from Dow Corning.

Results substantially comparable to those above can also be obtained when the suds suppressor is a microcrystalline wax having a melting point from 65°C to 100°C, and which is selected from petrolatum and oxidized petrolatum waxes, Fischer-Tropsch and oxidized Fischer-Tropsch waxes, ozokerite, ceresin, montan wax, beeswax, candelilla, and carnauba wax.

Substantially comparable results are obtained where the builder used in the paste-form detergent composition above is replaced by sodium or potassium pyrophosphate, metaphosphate, bicarbonate; an alkali metal salt of a polyacetate, carboxylate, polycarboxylate or a polyhydroxy sulfonate; sodium citrate, sodium oxydisuccinate, or sodium mellitate.

EXAMPLE II

A paste-form detergent composition for use in automatic dishwashers, having a viscosity of about 500,000 centipoise, and having the following composition is formulated:

Component	% by weight
Neodol 45-7	5.8
DB-544	0.8
Silicate solids (2.0r)	14.0
Triethanolamine	27.0
Anhydrous sodium tripoly-phosphate	35.0
SP-72[1]	0.6
Milezyme[2]	0.6
Water and minors	balance to 100

[1]A proteolytic enzyme available from Novo Industri A/S, Copenhagen, Denmark, which exhibits an activity of greater than 80% of its maximum activity when measured at pH 12 using the Anson hemoglobin method in the presence of urea.

[2]An amylolytic enzyme available from Miles Laboratories, Elkhart, Indiana, which exhibits activity greater than 50% of its maximum activity when measured at pH 8 by the SKB method at 37°C.

About 8 grams of this composition is placed in a water-soluble packet made of polyvinyl alcohol film, having a thickness of 2.5 mils. The packet is sealed by the heat and water method. This detergent article exhibits good dispensing and dissolution properties when used in an automatic dishwasher.

EXAMPLE III

A paste-form detergent composition for use in automatic dishwashers, having a viscosity of about 1,000,000 centipoise, and having the following composition, is formulated:

Component	% by weight
Ethylene oxide/propylene oxide condensate of trimethylol propane	25.0
Sodium cumene sulfonate	10.0
Silicate solids (2.0r)	12.0
Triethanolamine	19.0
Anhydrous sodium tripoly-phosphate	25.0
SP-88	0.8
Termamyl	0.4
Monostearyl acid phosphate	0.75
DB-544	0.25
Waters and minors	balance to 100

About 15 grams of this composition is placed in a water-soluble packet made of polyethylene oxide film, having a thickness of 1.5 mils. The packet is sealed ultrasonically. The detergent article is placed in the detergent dispenser cup of an automatic dishwasher, and dirty dishes and tableware are washed with it. The dishes and tableware are clean after the completion of the dishwasher cycle, and there is no residue of the paste or the packet remaining in the dispenser cup or on the inside of the dishwasher.

EXAMPLE IV

A gel-form detergent composition for use in automatic dishwashers, having the following composition, is formulated:

Component	% by weight
TAE_9	7.9
Silicate solids (2.0r)	32.0
Sodium tripolyphosphate	19.8
SP-88	0.4
Termamyl	0.8
Waters and minors	balance to 100

About 12 grams of this composition is placed in a water-soluble packet made of a medium hydrolysis polyvinyl alcohol film, commercially available from Monosol, having a thickness of about 1.5 mils. The packet is heat-sealed. This detergent article exhibits good cleaning, dispensing and solubilizing properties when used in an automatic dishwasher.

EXAMPLE V

The following three paste-form detergent compositions for use in automatic dishwashers, having the following compositions, are formulated:

Component	% by weight		
	A	B	C
Neodol 45-7	7.2	7.2	7.2
Polyethyleneglycol 400	20.4	-	-
Neodol 23 alcohol	-	20.4	-
Mineral oil	-	-	20.4
Silicate solids (2.4r)	21.4	21.4	21.4
Silicate solids (2.0r)	4.36	4.36	4.36
Sodium tripolyphosphate	25.5	25.5	25.5
Sodium carbonate	9.2	9.2	9.2
Water	8.4	8.4	8.4
Dye	0.04	0.04	0.04
Perfume	0.3	0.3	0.3
Enzyme (SP-72 encapsulated in polyethyleneglycol 6000)	3.2	3.2	3.2

Each of the above paste-form detergent compositions (about 10 grams of each) is sealed in water-soluble packets made of Edisol-M®, a methyl cellulose film, having a thickness of about 1.5 mils, commercially available from Polymer Films, Inc. The packets are heat-sealed. Each of these detergent articles exhibits good cleaning, dispensing and solubilization properties, when placed in the detergent dispenser cup and used in an automatic dishwasher.

What is claimed is:

1. An article for cleaning tableware and cookware in an automatic dishwasher, consisting essentially of a packet made up of a water-soluble material in film-form, enclosing within it a paste-form, automatic dishwasher-compatible detergent composition.

2. An article according to Claim 1 wherein the paste-form detergent composition has a viscosity of at least about 1000 centipoise.

3. An article according to Claim 2 wherein the packet is made of a water-soluble material selected from the group consisting of polyvinyl alcohol, polyethylene oxide, and methyl cellulose.

4. An article according to Claim 3 wherein the water-soluble film has a thickness of from about 1 to about 3 mils.

5. An article according to Claim 4 wherein the detergent composition contains at least about 0.5% by weight of an alkoxylated nonionic surface-active agent, wherein said alkoxy moiety is selected from the group consisting of ethylene oxide, propylene oxide and mixtures thereof.

6. An article according to Claim 5 wherein the detergent composition contains from about 1% to about 40% of said alkoxylated nonionic surface-active agent.

7. An article according to Claim 6 wherein said alkoxylated nonionic surface-active agent is selected from the group consisting of the condensation product of one mole of tallow alcohol with from about 6 to about 20 moles of ethylene oxide; an alkoxylate having the formula

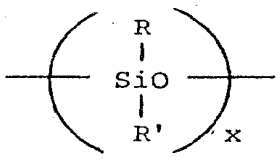
$$Y[(C_3H_6O)_n(C_2H_4O)_mH]_x$$

wherein x has a value of at least about 2, n has a value such that the molecular weight of the polyoxypropylene hydrophobic base is at least 900 and m has a value such that the oxyethylene content of the molecule is from about 10% to 90% by weight, and wherein Y is selected from the group consisting of propylene glycol, glycerine, pentaerythritol, trimethylolpropane, ethylenediamine and mixtures thereof; and mixtures of these surface-active agents.

8. An article according to Claim 7 wherein the detergent composition contains from 0.001% to about 5% by weight of a suds-regulating agent.

9. An article according to Claim 8 wherein said suds-regulating agent is selected from the group consisting of

(a) a siloxane having the formula:



wherein x is from about 20 to about 2,000 and R and R' are each alkyl or aryl groups;

(b) A microcrystalline wax having a melting point in the range from about 35°C to about 115°C and a saponification value of less than 100;

(c) an alkyl phosphate ester component selected from the group consisting of stearyl acid phosphate and oleyl acid phosphate;

(d) a self-emulsified silicone suds suppressor; and

(e) mixtures thereof.

10. An article according to Claim 9 wherein the detergent composition contains an enzyme component selected from the group consisting of high alkaline activity proteases, high alkaline activity amylases and mixtures thereof.

11. An article according to Claim 10 wherein the enzyme component is a mixture of protease and amylase and said amylase is one cultivated from a strain of bacillus lichenformis selected from the group consisting of NCIB 8061, NCIB 8059, ATCC 6334, ATCC 6598, ATCC 11945, ATCC 8480, ATCC 9945A and mixtures thereof.

12. An article according to Claim 11 wherein said protease is one cultivated from a bacterium strain selected from the group consisting of NCIB 10317, NCIB 10147, NCIB 10313, NCIB 10315, NRRL B 1107 and mixtures thereof.

13. An article according to Claim 12 wherein the ratio of protease to amylase is from about 2:1 to 1:2 by weight.

14. A process for cleaning tableware and cookware items in an automatic dishwasher comprising washing said items in an agitated aqueous solution to which has been added an article consisting essentially of a packet made up of a water-soluble material in film-form, enclosing within it a paste-form, automatic dishwasher-compatible detergent composition.

15. A process according to Claim 14 wherein said article is added to the aqueous washing solution by the detergent dispenser in the automatic dishwasher.

16. A process according to Claim 15 wherein the paste-form detergent composition has a viscosity of at least about 1000 centipoise.

17. A process according to Claim 16 wherein the packet is made of a water-soluble material selected from the group consisting of polyvinyl alcohol, polyethylene oxide, and methyl cellulose.

18. A process according to Claim 17 wherein the water-soluble film has a thickness of from about 1 to about 3 mils.

19. A process according to Claim 18 wherein the detergent composition contains at least about 0.5% by weight of an alkoxylated nonionic surface-active agent, wherein said alkoxy moiety is selected from the group consisting of ethylene oxide, propylene oxide and mixtures thereof.

20. A process according to Claim 19 wherein the detergent composition contains an enzyme component selected from the group consisting of high alkaline activity proteases, high alkaline activity amylases and mixtures thereof.

SJG:sp/pw

SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente